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United States Patent and Trademark Office

July 23, 2004

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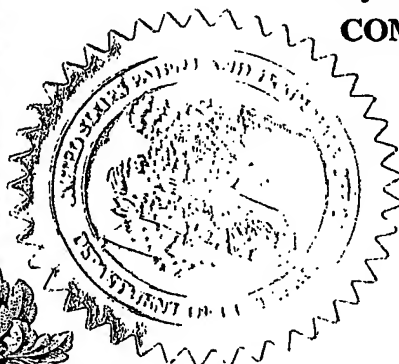
APPLICATION NUMBER: 60/489,121

FILING DATE: July 23, 2003

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

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PATENT APPLICATION SERIAL NO. _____

U.S. DEPARTMENT OF COMMERCE
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FEE RECORD SHEET

07/24/2003 KBETEMAI 00000025 033975 60489121
01 FC:1005 160.00 DA

PTO-1556
(5/87)

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label N .

INVENTOR(S)					
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)			
XIAORONG	YOU	Bear, DE			
<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
VISCOSITY REDUCIBLE RADIATION CURABLE RESIN COMPOSITION					
Direct all correspondence to:		CORRESPONDENCE ADDRESS			
<input checked="" type="checkbox"/> Customer Number		00909		→ Place Customer Number Bar Code Label here	
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ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification Number of Pages		19		<input type="checkbox"/> CD(s), Number	
<input type="checkbox"/> Drawing(s) Number of Sheets				<input type="checkbox"/> Other (specify)	
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				FILING FEE AMOUNT (\$)	
<input type="checkbox"/> A check or money order is enclosed to cover the filing fees					
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:				033975	
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.				160.00	
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/> No.					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

Respectfully submitted,

SIGNATURE

TYPED or PRINTED NAME Paul L. Sharer

TELEPHONE (703) 905-2180

Date

Jul 23, 2003

REGISTRATION NO.

(if appropriate)

Docket Number:

36004

021028-0305216

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S.D. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

17058 U.S. PTO
60/489121
07/23/03

FEE TRANSMITTAL for FY 2003

Effective 01/01/2003. Patent fees are subject to annual revision.

☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$ 160.00

Complete if Known

Application Number
Filing Date July 23, 2003
First Named Inventor XIAORONG YOU
Examiner Name
Art Unit
Attorney Docket No. 021028-0305216

METHOD OF PAYMENT (check all that apply)

☐ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None

☒ Deposit Account:

Deposit Account Number 033975
Deposit Account Name PILLSBURY WINTHROP LLP

The Commissioner is authorized to: (check all that apply)

☒ Charge fee(s) indicated below ☒ Credit any overpayments
☒ Charge any additional fee(s) during the pendency of this application
☐ Charge fee(s) indicated below, except for the filing fee to the above-identified deposit account.

FEE CALCULATION

1. BASIC FILING FEE

Large Entity	Small Entity	Fee Code (\$)	Fee Code (\$)	Fee Description	Fee Paid
1001	2001	750	375	Utility filing fee	
1002	2002	330	165	Design filing fee	
1003	2003	520	260	Plant filing fee	
1004	2004	750	375	Reissue filing fee	
1005	2005	180	80	Provisional filing fee	160.00

SUBTOTAL (1) (\$ 160.00

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

Total Claims -20** = ☐ X ☐ Fee Paid
Independent Claims -3** = ☐ X ☐ Fee Paid
Multiple Dependent

Large Entity	Small Entity	Fee Code (\$)	Fee Code (\$)	Fee Description	Fee Paid
1202	2202	18	9	Claims in excess of 20	
1201	2201	84	42	Independent claims in excess of 3	
1203	2203	280	140	Multiple dependent claim, if not paid	
1204	2204	84	42	** Reissue independent claims over original patent	
1205	2205	18	9	** Reissue claims in excess of 20 and over original patent	

SUBTOTAL (2) (\$

**or number previously paid, if greater; For Reissues, see above

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity	Small Entity	Fee Code (\$)	Fee Code (\$)	Fee Description	Fee Paid
1051	2051	130	65	Surcharge - late filing fee or oath	
1052	2052	50	25	Surcharge - late provisional filing fee or cover sheet	
1053	2053	130	65	Non-English specification	
1812	2520	2,520	1,260	For filing a request for ex parte reexamination	
1804	920*	920	460	Requesting publication of SIR prior to Examiner action	
1805	1,840*	1,840	920	Requesting publication of SIR after Examiner action	
1251	2251	110	55	Extension for reply within first month	
1252	2252	410	205	Extension for reply within second month	
1253	2253	930	465	Extension for reply within third month	
1254	2254	1,450	725	Extension for reply within fourth month	
1255	2255	1,970	985	Extension for reply within fifth month	
1401	2401	320	160	Notice of Appeal	
1402	2402	320	160	Filing brief in support of an appeal	
1403	2403	280	140	Request for oral hearing	
1451	2451	1,510	755	Petition to institute a public use proceeding	
1452	2452	110	55	Petition to revive - unavoidable	
1453	2453	1,300	650	Petition to revive - unintentional	
1501	2501	1,300	650	Utility issue fee (or reissue)	
1502	2502	470	235	Design issue fee	
1503	2503	630	315	Plant issue fee	
1460	2460	130	65	Petitions to the Commissioner	
1807	2807	50	25	Processing fee under 37 CFR 1.17(q)	
1808	2808	180	90	Submission of Information Disclosure Stmt	
8021	2021	40	20	Recording each patent assignment per property (times number of properties)	
1809	2809	750	375	Filing a submission after final rejection (37 CFR 1.129(a))	
1810	2810	750	375	For each additional invention to be examined (37 CFR 1.129(b))	
1801	2801	750	375	Request for Continued Examination (RCE)	
1802	2802	900	450	Request for expedited examination of a design application	

Other fee (specify)

*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) (\$ 0.00

SUBMITTED BY

Name (Print/Type) Paul L. Sharer
Signature

Registration No. (Attorney/Agent) 36004

(Complete if applicable)

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Date July 23, 2003

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VISCOSITY REDUCIBLE RADIATION CURABLE RESIN COMPOSITION.

FIELD OF THE INVENTION

The invention relates to viscosity reducible radiation curable resin compositions,
5 their use in methods for making three dimensional objects.

BACKGROUND IN THE INVENTION

Viscosity reducible radiation curable resin compositions are known from US
5,474,719 (which is incorporated herein by reference). Compositions have been
10 disclosed comprising materials that induce thixotropic flow behavior. The compositions
have a high viscosity at a low shear rate (for example 5,440 centipoise at 3 rpm, in a
Brookfield viscosity experiment), and a much lower viscosity at a higher shear rate (for
example 1,420 centipoise at 30 rpm). The difference in viscosity (centipoise) reported is
between about 2 and 4 at these shear rates. These compositions are pastes in the
15 absence of shear. US 20020195747 discloses a new solid freeform fabrication
apparatus to form three-dimensional objects from highly viscous paste-like materials.
These pastes contain fillers and have viscosities of greater than 10,000 centipoise at
ambient conditions. These paste materials cannot be handled in an ordinary
stereolithography machine, designed to handle liquid resins.

20

OBJECT OF THE INVENTION

It is an object of the present invention to provide radiation curable compositions
that contain an inorganic filler, show thixotropic behavior and have a low yield stress.
These compositions preferably show excellent storage and application stability.

25 It is another object of the present invention to provide a composition that has
thixotropic characteristics, contains at least one filler, and can be applied in a
conventional SL-machine to make three dimensional objects.

SUMMARY OF THE INVENTION.

30 The present invention relates to a viscosity reducible radiation curable
composition comprising at least one radiation curable component and a filler, wherein
the composition has the properties:

a yield stress value of $< 1100 \text{ Pa}$,

a viscosity (at a shear rate of 1 sec^{-1}) between 1 and $1500 \text{ Pa}\cdot\text{sec}$, and

a filler settling speed less than 0.3 mm/day.

A second embodiment of the present invention is a viscosity reducible radiation curable composition comprising at least one radiation curable component and a filler, wherein the composition has the properties:

- 5 a yield stress value of < 1100 Pa,
- a viscosity (at a shear rate of 10 sec^{-1}) between 1 and 200 Pa.sec, and
- a filler settling speed less than 0.3 mm/day.

DETAILED DESCRIPTION OF THE INVENTION

- 10 The compositions of the present invention are radiation curable and contain at least one radiation curable component. Examples of radiation curable components are cationically polymerizable components, and radical polymerizable components.

(A) Cationic polymerizable component

- Cationic polymerizable component (hereinafter also referred to as
- 15 component (A)) is an organic compound that polymerizes or cross links in the presence of a cationic polymerization initiator when irradiated with light. Examples of cationic polymerizable components include epoxy compounds, oxetane compounds, oxolane compounds, cyclic acetal compounds, cyclic lactone compounds, thiirane compounds, thietane compounds, vinyl ether compounds and cyclic thioether compounds. Among
- 20 these compounds, the presence of epoxy compounds and/or oxetane compounds is preferred, because the curing rate of the prepared resin composition is high, and the cured resin obtained from the resin composition has good mechanical properties.

- Epoxy compounds which can be used as the component (A) include
- bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, bisphenol S diglycidyl ether,
- 25 brominated bisphenol A diglycidyl ether, brominated bisphenol F diglycidyl ether, brominated bisphenol S diglycidyl ether, epoxy novolak resin, hydrogenated bisphenol A diglycidyl ether, hydrogenated bisphenol F diglycidyl ether, hydrogenated bisphenol S diglycidyl ether, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate,
- 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy) cyclohexane-metha-dioxane,
- 30 bis(3,4-epoxycyclohexylmethyl) adipate, vinylcyclohexene oxide,
- 4-vinylepoxycyclohexane, bis(3,4-epoxy-6-methylcyclohexyl- methyl) adipate,
- 3,4-epoxy-6-methylcyclohexyl-3',4'-epoxy-6'-methyl cyclohexane carboxylate,
- methylenebis(3,4-epoxycyclohexane), dicyclopentadiene diepoxide, ethylene glycol
- di(3,4-epoxycyclohexylmethyl) ether, ethylene bis(3,4-epoxycyclohexanecarboxylate),

epoxy- hexahydrodioctyl phthalate, epoxyhexahydrophthalic acid di-2-ethylhexyl, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether; polyglycidyl ether of polyether polyol obtained by adding one or
 5 more kinds of alkylene oxide to an aliphatic polyhydric alcohol such as ethylene glycol, propylene glycol, and glycerol; diglycidyl ester of an aliphatic head chain dibasic acid; mono glycidyl ether of aliphatic higher alcohol; phenol, cresol, and butyl phenol and a monoglycidyl ether of the polyether alcohol obtained by adding an alkylene oxide to these; glycidyl ester of a higher fatty acid; epoxidated soybean oil, epoxy stearic acid
 10 butyl, epoxy stearic acid octyl, epoxidated linseed oil, and epoxidated polybutadiene, for example.

Among these compounds, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, hydrogenated bisphenol A diglycidyl ether, hydrogenated bisphenol F diglycidyl ether, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate,
 15 bis(3,4-epoxycyclohexylmethyl) adipate, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, polyethylene glycol diglycidyl ether, and polypropylene glycol diglycidyl ether are preferred.

Examples of oxetane compounds are trimethylene oxide, 3,3-dimethyl
 20 oxetane, 3,3-dichloro methyl oxetane, 3-ethyl-3-phenoxy methyl oxetane, bis(3-ethyl-3-methyloxy) butane, 3-ethyl-3-hydroxymethyloxetane, 3-(meth)allyloxymethyl-3-ethyloxetane, (3-ethyl-3-oxetanylmethoxy)methylbenzene, (3-ethyl-3-oxetanylmethoxy)benzene, 4-fluoro-[1-(3-ethyl-3-oxetanylmethoxy)methyl]-benzene, 4-methoxy-[1-(3-ethyl-3-oxetanylmethoxy)methyl]benzene, [1-(3-ethyl-3-oxetanylmethoxy)ethyl] phenyl ether, isobutoxymethyl (3-ethyl-3-oxetanylmethyl) ether,
 25 isobornyloxyethyl (3-ethyl-3-oxetanylmethyl) ether, isobornyl (3-ethyl-3-oxetanylmethyl) ether, 2-ethylhexyl (3-ethyl-3-oxetanyl methyl) ether, ethyldiethylene glycol (3-ethyl-3-oxetanylmethyl) ether, dicyclopentadiene (3-ethyl-3-oxetanylmethyl) ether, dicyclopentenyl (3-ethyl-3-oxetanylmethyl) ether, tetrahydrofurfuryl (3-ethyl-3-oxetanylmethyl) ether,
 30 tetrabromophenyl (3-ethyl-3-oxetanylmethyl) ether, 2-tetrabromophenoxyethyl (3-ethyl-3-oxetanylmethyl) ether, tribromophenyl (3-ethyl-3-oxetanylmethyl) ether, 2-tribromophenoxyethyl (3-ethyl-3-oxetanylmethyl) ether, 2-hydroxyethyl (3-ethyl-3-oxetanyl methyl) ether, 2-hydroxypropyl (3-ethyl-3-oxetanylmethyl) ether, butoxyethyl (3-

ethyl-3-oxetanylmethyl) ether, pentachlorophenyl (3-ethyl-3-oxetanylmethyl) ether, pentabromophenyl (3-ethyl-3-oxetanylmethyl) ether, bornyl (3-ethyl-3-oxetanylmethyl) ether, 2-phenyl-3, 3-dimethyl-oxetane, and 2-(4-methoxyphenyl)-3, 3-dimethyl-oxetane.

Oxetanes containing two or more oxetane rings in the molecule include, for instance, 3,7-bis(3-oxetanyl)-5-oxa-nonane, 3,3'-(1,3-(2-methylenyl)propanediylbis(oxymethylene))bis-(3-ethyloxetane), 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene, 1,2-bis[(3-ethyl-3-oxetanylmethoxy)methyl]ethane, 1,3-bis[(3-ethyl-3-oxetanylmethoxy)methyl]propane, ethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether, dicyclopentenyl bis(3-ethyl-3-oxetanylmethyl) ether, triethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether, tetraethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether, tricyclodecanediyl dimethylene (3-ethyl-3-oxetanylmethyl) ether, trimethylolpropane tris(3-ethyl-3-oxetanylmethyl) ether, 1,4-bis(3-ethyl-3-oxetanylmethoxy)butane, 1,6-bis(3-ethyl-3-oxetanylmethoxy)hexane, pentaerythritol tris(3-ethyl-3-oxetanylmethyl) ether, pentaerythritol tetrakis(3-ethyl-3-oxetanylmethyl) ether, polyethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether, dipentaerythritol hexakis(3-ethyl-3-oxetanylmethyl) ether, dipentaerythritol pentakis(3-ethyl-3-oxetanylmethyl) ether, dipentaerythritol tetrakis(3-ethyl-3-oxetanylmethyl) ether, caprolactone-modified dipentaerythritol hexakis(3-ethyl-3-oxetanylmethyl) ether, caprolactone-modified dipentaerythritol pentakis(3-ethyl-3-oxetanylmethyl) ether, ditrimethylolpropane tetrakis(3-ethyl-3-oxetanylmethyl) ether, ethoxylated bisphenol A bis(3-ethyl-3-oxetanylmethyl) ether, propoxylated bisphenol A bis(3-ethyl-3-oxetanylmethyl) ether, ethoxylated hydrogenated bisphenol A bis(3-ethyl-3-oxetanylmethyl) ether, propoxylated hydrogenated bisphenol A bis(3-ethyl-3-oxetanylmethyl) ether, ethoxylated bisphenol F (3-ethyl-3-oxetanylmethyl) ether.

Examples of commercially available cationic polymerizable organic compounds include UVR-6100, UVR-6105, UVR-6110, UVR-6128, UVR-6200, and UVR-6216 (Union Carbide Corp.); Celoxide 2021, Celoxide 2021P, Celoxide 2081, Celoxide 2083, Celoxide 2085, Celoxide 2000, Celoxide 3000, Glycidole, AOEX24, Cyclomer A200, Cyclomer M100, Epolead GT-300, Epolead GT-301, Epolead GT-302, Epolead GT-400, Epolead 401, and Epolead 403 (Daicel Co., Ltd.); Epicoat 828, Epicoat 812, Epicoat 1031, Epicoat 872, and Epicoat CT508 (Yuka Shell Company); KRM-2100, KRM-2110, KRM-2199, KRM-2400, KRM-2410, KRM-2408, KRM-2490, KRM-2200, KRM-2720, KRM-2750 (Asahi Denka Kogyo K.K.); Rapi-Cure DVE-3, CHVE, and PEPC (ISP Company); and VECTOMER 2010, 2020, 4010, and 4020 (Allied Signal Company).

The above cationic polymerizable compounds can be used singly or in combinations of two or more.

The component(A) content of the resin composition of this invention can be within the range of 10 to 95 wt%, preferably 30 to 90 wt%, and more preferably 40 to 85 wt%.

(B) Cationic photopolymerization initiator

When a cationically polymerizable component A is present, the composition preferably also contains a cationic photopolymerization initiator (B). In the compositions according to the invention, any type of photoinitiator that, upon exposure to actinic radiation, forms cations that initiate the reactions of the cationically polymerizable component (A) can be used. There are a large number of known and technically proven cationic photoinitiators for epoxy resins that are suitable. They include, for example, onium salts with anions of weak nucleophilicity. Examples are halonium salts, iodosyl salts or sulfonium salts, such as are described in published European patent application EP 153904 and WO 98/28663, sulfoxonium salts, such as described, for example, in published European patent applications EP 35969, 44274, 54509, and 164314, or diazonium salts, such as described, for example, in U.S. Patents 3,708,296 and 5,002,856. Other cationic photoinitiators are metallocene salts, such as described, for example, in published European applications EP 94914 and 94915.

A survey of other current onium salt initiators and/or metallocene salts can be found in "UV Curing, Science and Technology", (Editor S. P. Pappas, Technology Marketing Corp., 642 Westover Road, Stamford, Conn., U.S.A.) Or "Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints", Vol. 3 (edited by P. K. T. Oldring). A preferred cationic photoinitiator (B) is an onium salt represented by the following general formula.



In the above formula, the cation is onium; Z represents S, Se, Te, P, As, Sb, Bi, O, I, Br, Cl, or N≡N; and R¹, R², R³ and R⁴ represent the same or different organic acid. a, b, c, and d are each an integer from 0 to 3, (a+b+c+d) being equal to the valence of Z. M represents a metal or metalloid that is the central atom of the halide complex; B, P, As, Sb, Fe, Sn, Bi, Al, Ca, In, Ti, Zn, Sc, V, Cr, Mn, and Co, for example. X represents a halogen. m is the net electric charge of the halide complex ion. n is the number of halide

atoms in the halide complex ion.

Examples of the anion (MX_n) in the above general formula include tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), hexafluoroantimonate (SbF_6^-), hexafluoroarsenate (AsF_6^-), and hexachloroantimonate ($SbCl_6^-$).

In addition, onium salts having an anion represented by a general formula $[MX_n(OH)]^-$ can be used. Further, onium salts having other anions such as perchloric acid ion (ClO_4^-), trifluoromethane sulfonic acid ion ($CF_3SO_3^-$), fluorosulfone acid ion (FSO_3^-), toluene sulfonic acid ion, trinitrobenzene sulfonic acid ion, and trinitrotoluene sulfonic acid ion can also be used.

Commercially available cationic photopolymerization initiators that can be preferably used as the component(B) include UVI-6950, UVI-6970, UVI-6974, and UVI-6990 (Union Carbide Corp.); Adekaoptomer SP-150, SP-151, SP-170, and SP-171 (Asahi Denka Kogyo K.K.); Irgacure 261 (Ciba Geigy); CI-2481, CI-2624, CI-2639, and CI-2064 (Nihon Soda Co., Ltd.); CD-1010, CD-1011, and CD-1012 (Satomer Co., Ltd.); DTS-102, DTS-103, NAT-103, NDS-103, TPS-103, MDS-103, MPI-103, and BBI-103 (Green Chemical Co., Ltd.). Among these, UVI-6970, UVI-6974, Adeka Optomer SP-170, SP-171, CD-1012, and MPI-103 are especially preferable, because they impart a high photocuring sensitivity to the prepared resin composition.

The above cationic photopolymerization initiators may be used singly or in combinations of two or more.

The component(B) content of the resin composition of this invention may be within the range of 0.1 to 10 wt%, preferably 0.2 to 5 wt%, and more preferably 0.3 to 3 wt%.

(C) radical polymerizable component

The present invention may comprise one or more free radical curable components, e.g. one or more free radical polymerizable components having one or more ethylenically unsaturated groups, such as (meth)acrylate (i.e. acrylate and/or methacrylate) functional components. The free radical polymerizable components may have one or more radically polymerizable groups.

Non-limiting examples of monofunctional (meth)acrylates are isobornyl (meth)acrylate, lauryl (meth)acrylate, and phenoxyethyl (meth)acrylate.

Commercially available mono-functional monomers include Aronix M-101, M-102, M-111, M-113, M-117, M-152, and TO-1210 (Toagosei Chemical Industry Co., Ltd.), KAYARAD TC-110S, R-564, and R-128H (Nippon Kayaku Co., Ltd.), Viscoat 192,

Viscoat 220, Viscoat 2311HP, Viscoat 2000, Viscoat 2100, Viscoat 2150, Viscoat 8F, and Viscoat 17F (Osaka Organic Chemical Industry, Ltd.).

Polyfunctional monomers which can be used for the component(C) are ethylene glycol di(meth)acrylate, dicyclopentenyl di(meth)acrylate, triethylene glycol diacrylate, tetra ethylene glycol di(meth)acrylate, tricyclodecanediyl dimethylene di(meth)acrylate, tris(2-hydroxyethyl) isocyanurate di(meth)acrylate, tris(2-hydroxyethyl) isocyanurate tri(meth)acrylate, caprolactone-modified tris(2-hydroxyethyl) isocyanurate tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, ethylene oxide (hereinafter also referred to as EO for short)-modified trimethylolpropane tri(meth)acrylate, propylene oxide (hereinafter also referred to as PO for short)-modified trimethylolpropane tri(meth)acrylate, tripropylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, bisphenol A diglycidyl ether with (meth)acrylic acid adducts at both terminals, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, polyester di(meth)acrylate, polyethylene glycol di(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol tetra(meth)acrylate, caprolactone-modified dipentaerythritol hexa(meth)acrylate, caprolactone-modified dipentaerythritol penta(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, EO-modified bisphenol A di(meth)acrylate, PO-modified bisphenol A di(meth)acrylate, EO-modified hydrogenated bisphenol A di(meth)acrylate, PO-modified hydrogenated bisphenol A di(meth)acrylate, EO-modified bisphenol F di(meth)acrylate, and (meth)acrylate of phenolnovolac polyglycidyl ether.

Commercially available polyfunctional monomers include SA1002 (Mitsubishi Chemical Corp.); Viscoat 195, Viscoat 230, Viscoat 260, Viscoat 215, Viscoat 310, Viscoat 214HP, Viscoat 295, Viscoat 300, Viscoat 360, Viscoat GPT, Viscoat 400, Viscoat 700, Viscoat 540, Viscoat 3000, and Viscoat 3700 (Osaka Organic Chemical Industry, Ltd.); KAYARAD R-526, HDDA, NPGDA, TPGDA, MANDA, R-551, R-712, R-604, R-684, PET-30, GPO-303, TMPTA, THE-330, DPHA, DPHA-2H, DPHA-2C, DPHA-2I, D-310, D-330, DPCA-20, DPCA-30, DPCA-60, DPCA-120, DN-0075, DN-2475, T-1420, T-2020, T-2040, TPA-320, TPA-330, RP-1040, RP-2040, R-011, R-300, and R-205 (Nippon Kayaku Co., Ltd.); Aronix M-210, M-220, M-233, M-240, M-215, M-305, M-309, M-310, M-315, M-325, M-400, M-6200, and M-6400 (Toagosei Chemical Industry Co., Ltd.); Light acrylate BP-4EA, BP-4PA, BP-2EA, BP-2PA, and DCP-A (Kyoetsiya Chemical Co., Ltd.); New Frontier BPE-4, TEICA, BR-42M, and

GX-8345 (Daiichi Kogyo Seiyaku Co., Ltd.), ASF-400 (Shin Nippon Steel Chemical Co., Ltd.); Repoxy SP-1506, SP-1507, SP-1509, VR-77, SP-4010, and SP-4060 (Showa Highpolymer Co., Ltd.); and NK ester A-BPE-4 (Shin-Nakamura Chemical Co., Ltd.).

A polyfunctional monomer having three or more functional monomers for this purpose can be selected from any of the above described tri(meth)acrylate compounds tetra(meth)acrylate compounds, penta(meth)acrylate compounds, and hexa(meth)acrylate compounds. Among them, trimethylolpropane tri(meth)acrylate, EO-modified trimethylolpropane tri(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, and ditrimethylolpropane tetra(meth)acrylate are especially preferable.

Monofunctional and polyfunctional monomers of component (C) may be used singly or in combinations of two or more, such that the amount of component (C) is preferably 5 to 50 wt%, alternatively 7 to 25 wt%, and more preferably 10 to 20 wt%.

15 (D) Radical photopolymerization initiator

When a radically polymerizable component C is present, the composition preferably also contains a radical photopolymerization initiator (D). In the compositions according to the invention, any type of photoinitiator that, upon exposure to actinic radiation, forms radicals that initiate the reactions of the radically polymerizable component (C) can be used.

Radical photopolymerization initiators which can be used for the component(D) include etophenone, acetophenone benzyl ketal, anthraquinone, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, carbazole, xanthone, 4-chlorobenzo-phenone, 4,4'-diaminobenzophenone, 1,1-dimethoxydeoxy-benzoin, 3,3'-dimethyl-4-methoxybenzophenone, thioxanethone compounds, 2-methyl-1-4-(methylthio) phenyl-2-morpholinopropan-2-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, triphenylamine, 2,4,6-trimethylbenzoyl diphenylphosphine oxides, bis(2,6-dimethoxybenzoyl)-2,4,4-tri-methylpentyl phosphone oxide, benzyl methyl ketal, 1-hydroxycyclohexylphenyl ketone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, fluorenone, fluorene, benzaldehyde, benzoin ethyl ether, benzoin propyl ether, benzophenone, Michler's ketone, 3-methylacetophenone, 3,3',4,4'-tetra(t-butylperoxycarbonyl) benzophenone (BTTB), and combination of BTTB and a color sensitizer such as xanthene, thioxanthene, cumarin, and ketocumarin, for

example. Among these compounds, benzyl methyl ketal, 1-hydroxycyclohexylphenyl ketone, 2,4,6-trimethylbenzoyl diphenylphosphine oxides, and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one are especially preferable.

The above radical photopolymerization initiators may be used singly or in combinations of two or more.

The component(D) content of the liquid of the resin composition of this invention is within the range of 0.01 to 10 wt% and preferably 0.1 to 8 wt%. If the amount of the component(D) is too small, the radical polymerization rate of the prepared resin composition (curing rate) becomes too low, and hence a longer time is required for laminate fabricating, or the dimensional accuracy decreases. On the other hand, if the amount of the component(D) is too large, the surplus amount of the radical photopolymerization initiator exerts a bad influence on the curing properties of the prepared resin composition and on the mechanical properties, heat resistance, and ease of handling.

15

(E) Filler

The filler (hereinafter also referred to as the component(E)) of the resin composition of this invention may be any substance without special limitation, but an inorganic substance is preferred from the point of view of the water-resisting capabilities and mechanical properties of the fibrous material forming molds made of the prepared resin composition. The filler may be present as particles of any form, or for example powders.

For example, silica powder with an average particle size or fiber length of 1 to 50 μm , such as of fused silica and/or crystalline silica may be used. Another example of a suitable filler is fused and/or crystalline silica, of which the powder particles are spherical.

Inorganic filler substances other than silica powder include polymers, minerals, metals, metallic compounds, ceramics, or any combination thereof. Some polymers that may be used are thermoplastics such as ABS, Nylon, polypropylene, polycarbonate, polyethersulfate, and the like. Some metallic powders or particles that may be used are steel, steel alloy, stainless steel, aluminum, aluminum alloy, titanium, titanium alloy, copper, tungsten, tungsten carbide, molybdenum, nickel alloy, lanthanum, hafnium, tantalum, rhenium, rubidium, bismuth, cadmium, indium, tin, zinc, cobalt, manganese, chromium, gold, silver, and the like. Some ceramics that may be used are

aluminum nitride, aluminum oxide, calcium carbonate, fluoride, magnesium oxide, silicon carbide, silicon dioxide, silicon nitride, titanium carbide, titanium carbonitride, titanium diboride, titanium dioxide, tungsten carbide, tungsten trioxide, zirconia, and zinc sulphide, and the like. Some rare earth mineral powders that may be used are cerium
 5 oxide, dysprosium oxide, erbium oxide, gadolinium oxide, holmium oxide, lutetium oxide, samarium oxide, terbium oxide, yttrium oxide, and the like. glass powder, alumina, alumina hydrate, magnesium oxide, magnesium hydroxide, barium sulfate, calcium sulfate, calcium carbonate, magnesium carbonate, silicate mineral, diatomaceous earth, silica sand, silica powder, oxidation titanium, aluminum powder, bronze, zinc powder,
 10 copper powder, lead powder, gold powder, silver dust, glass fiber, titanate potassium whiskers, carbon whiskers, sapphire whiskers, vermicular whiskers, boron carbide whiskers, silicon carbide whiskers, and silicon nitride whiskers.

The condition of the surface of the particles of the filler used and the impurities contained in filler from the manufacturing process can affect the curing
 15 reaction of the resin composition. In such cases, it is preferable to wash the filler particles or coat the particles with an appropriate primer as a method of improving the curing properties.

These inorganic fillers may also be surface-treated with a silane coupling agent. Silane coupling agents which can be used for this purpose include vinyl
 20 trichlorosilane, vinyl tris (β -methoxyethoxy) silane, vinyltriethoxy silane, vinyltrimethoxy silane, γ -(methacryloxypropyl)trimethoxy silane, β -(3,4-epoxycyclohexyl)ethyltrimethoxy silane, γ -glycidyloxypropyltrimethoxy silane, γ -glycidyloxypropylmethyl diethoxy silane, N- β -(aminoethyl)- γ -aminopropyltrimethoxy silane, N- β -(aminoethyl)- γ -aminopropylmethyldimethoxy silane, γ -aminopropyltriethoxysilane, N-phenyl- γ -amino
 25 propyl trimethoxy silane, γ -mercaptopropyl trimethoxysilane, and γ -chloropropyltrimethoxy silane.

The above inorganic fillers may be used singly or in combination of two or more. By using inorganic fillers with different properties in combination, it is possible to impart the desirable properties derived from the fillers to the prepared resin composition.
 30 Further, the prepared resin composition can have a remarkably different fluidity if the grain size or fiber length distribution of the inorganic filler used is different, though the substance, the average grain size or fiber length, and the amount are the same. Therefore, by appropriately determining not only the average grain size or fiber length but also the grain size or fiber length distribution, or by using inorganic fillers of the same

substance with different average grain sizes or fiber lengths in combination, the necessary amount of the filler and the fluidity and other properties of the prepared resin can be controlled as desired.

The component(E) content of the resin composition of this invention is
 5 within the range of 10-95 wt%, preferably 30 to 80 wt% and more preferably 50 to 70 wt% of the total composition.

(F) Thixotropic agent

The resin composition of the present invention contains a material that
 10 acts as a thixotropic agent. Suitable thixotropic agents provide a stable resin, with no or limited settling of filler over time. Preferably the pH of the material is below pH 7, and it should have no or only limited influence on photospeed of the resins and mechanical properties of the parts made out of the resins by curing the resins with for example UV-light. Preferably the thixotropic agents show a fast recovery of viscosity, after application
 15 of shear in order to speed up the stereolithography process.

Examples of suitable thixotropic agents are polyvinylpyrrolidone (like PVP K-15, K30 and K-90), titanate coupling agents (like Ken-React LICA 38 and 55), aluminum distearate or aluminum tristearate, copolymers with acidic groups (like Disperbyk-111), compounds having ionic groups (like Centrol 3F SB, Centrol 3F UB and
 20 Emulmetik 120), fumed silica (like Aerosil 200), organic derivatives of castor oil (like Thixatrol 1, Thixatrol ST, Thixatrol GST and Thixcin R) and polyoxyethylene-polyoxypropylene block copolymers (like the Pluronic® series).
 Preferably the thixotropic agent is chosen from the group consisting of Thixcin R, Thixatrol 1, Thixatrol GST, Thixatrol ST, Aluminum stearate 132 and 22, MPA 14, Ken
 25 react LICA 38 and KR 55. Most preferred are thixotropic agents from the group consisting of Thixcin R, Thixatrol 1, Thixatrol GST and Thixatrol ST.

Thixotropic agents are added in sufficient amounts to prevent settling of the filler. Typically, the amount of thixotropic agent is between 0,1 and 10 wt% (relative to the total of the composition), preferably between 0.5 and 5 wt%.

30

(G) Flow aid

Addition of thixotropic agents in sufficient amounts to prevent settling of the filler, will generally give resins that have a high yield stress. The yield stress can be lowered, without adversely affecting the thixotropic and anti settling behavior of the resin,

by addition of a flow aid. Suitable flow aids are low molecular weight polyacrylates (like Modaflow 2100, LG-99, Resin flow LF and resin flow LV) or polyalkyleneoxide modified polydimethylsiloxane (like Silwet L 7602). Flow aids are added in an amount between 0.01 and 5 wt%, preferably between 0.02 and 1 wt%.

5

Optional components and additives

The resin composition of this invention may contain optional components other than the components (A) to (G) described above, within the limits that do not impair the photo-curing properties of the resin composition. The optional components include photosensitizer (polymerization promoters) consisting of amine compounds such as triethanolamine, methyl diethanolamine, triethylamine, and diethylamine; photosensitizers consisting of thioxanethone, derivatives of thioxanethone, anthraquinone, derivatives of anthraquinone, anthracene, derivatives of anthracene, perylene, derivatives of perylene, benzophenone, benzoin isopropyl ether; and reactive diluents such as vinyl ether, vinyl sulfide, vinyl urethane, urethane acrylate, and vinyl urea, for example.

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The resin composition of this invention may also contain various kinds of additives. Examples of suitable additives include resins or polymers such as epoxy resin, polyamide, polyamideimide, polyurethane, polybutadiene, polychloroprene, polyether, polyester, styrene/butadiene styrene block copolymer, petroleum resin, xylene resin, ketone resin, cellulose resin, fluorine containing oligomer, and silicon containing oligomer; polymerization inhibitors such as for example phenothiazine, and 2,6-di-t-butyl-4-methyl phenol; polymerization initiation assistants, leveling agents, wettability improvers, surfactants, plasticizers, UV absorbers, silane coupling agents, resin particles, pigment, and dyes.

20
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The resin composition of this invention can be prepared by mixing the above described components (A) to (D), (F) and (G), optional components, and additives into a homogenous resin solution and then dispersing the filler component (E) in the homogeneous resin solution.

30

The invention also relates to a method for forming a three dimensional object comprising the steps of:

- a) Coating a layer of a viscosity reduced composition on a surface;
- b) Allowing said layer to become a viscosity reducible composition layer having a viscosity greater than said viscosity reduced layer;

- c) Exposing said viscosity reducible layer to radiation imagewise by radiation means in order to photoform said layer imagewise;
- d) repeating steps a) through c) until the three dimensional object is being formed.

5 Test methods

The following test method is used to measure the yield stress and viscosity vs. shear rate of paste samples of the present invention. Measurements are performed on a SR5 Stress Rheometer, mfg by Rheometric Scientific Inc. the following settings are used:

- 10 Test Type: Stress sweep in steady rotation mode.
- Geometry: Parallel plate, 25 mm diameter and 1.0 mm gap.
- Temperature: 25°C, regulated by a bottom Peltier plate.
- Sweep mode: Logarithmic, 10 points per decade.
- Initial Stress: 20 Pa.
- 15 Final Stress: 10^4 Pa.
- Maximum time per data point: 15 seconds.
- Delay time: 10-second delay before starting test.

- The technique for sample loading is standard, known by one skilled in rheometer use. When the sample has been loaded and excess material trimmed from the plate edges, the run is started. The run creates three kinds of graphs: (1) Shear rate vs. shear stress, log-log scales; (2) Shear stress vs. shear rate, both scales linear; and (3) Viscosity vs. shear rate, log-log scales. The yield point is defined as the point in the shear-rate vs shear stress curve (1) where the rate equals 10^{-2} sec^{-1} . The yield stress is defined as the shear stress at which the shear rate first exceeds $1 \times 10^{-2} \text{ sec}^{-1}$. The plot of viscosity vs. shear rate (3) does not come from a separate experiment, but from a replotting of data already present in the original data set. A set of points relating shear stress and shear rate are already on hand. Viscosity is defined as shear stress divided by shear rate, so viscosity is calculated by the program and is available for plotting.

Test method to determine the recovery time (example 2)

Recovery measurements were performed with a Rheometric Scientific ARES-LS dynamic mechanical analyzer equipped with a concentric cylinder geometry. The cylinder diameters were 25 and 27 mm, respectively.

Before loading into the concentric cylinder system the samples were manually stirred for at least 1 minute. After loading the sample, a so-called steady shear experiment was performed with a shear rate of 110 1/s and a duration of 15 seconds. Immediately after this steady shear experiment, the instrument was switched to dynamic mode and a so-called time sweep with a fixed angular frequency of 1 rad/s and a strain amplitude of 0.3% was started. During this time sweep, the dynamic viscosity and the phase angle were monitored as a function of time to monitor the recovery of the sample structure. The test temperature was 23°C.

Determination of sedimentation rate.

The sedimentation rate of the formulations is determined as follows: Test tubes (dimensions height 150mm, outer diameter 20mm and inner diameter 17mm) are filled with the freshly prepared paste-like compositions up to level of 120mm (one tube for every composition). The test tubes are stored at room temperature in a draught-free place protected from light and the level of the clear solution on the top of the resin in each of the test tubes is measured every 24 hours. The settling speed is determined by measuring the settling during 15 days, and determining the average sedimentation per day with regression analysis.

Example 1—Effect of flow aid on yield stress

A paste-like composition is prepared by mixing the below components.

Component	Chemical Name	Component
UVR-1500	3,4-Epoxy Cyclohexyl Methyl-3,4-Epoxy Cyclohexyl Carboxylate	Epoxide
Heloxy 67	1,4-butanediol diglycidyl ether	Epoxide
SR-351	1,1,1-Trimethylolpropane triacrylate	Acrylate

DPHA	Dipentaerythritol hexaacrylate	Acrylate
Ir-184	1-Hydroxycyclohexyl phenyl ketone	Free Radical Initiator
CPI 6976	Sulfonium,(thiodi-4,1-phenylene)bis[diphenyl-bis[(OC-6-11)hexafluoroantimonate(1-)]]	Cationic Initiator
4-methoxyphenol	4-methoxyphenol	Additive
Vinyltrimethoxysilane	Vinyltrimethoxysilane	Additive
NP-100	Amorphous Silica Oxide	Filler
Aerosol 200	Amorphous Silica Oxide	Filler
Thixatrol ST	Organic derivative of castor oil based additive	Thixotropic agent
Thixin R	Organic derivative of castor oil based additive	Thixotropic agent
LG-99	Acrylic Polymer (Estron Chemical)	Flow aid
Modaflow 2100	Ethyl acrylate-2-ethylhexyl acrylate copolymer	Flow aid

A base composition is made by mixing 23.4 wt% UVR-1500, 8.74 wt% Heloxy 67, 3.91 wt% SR-351, 2.42 wt% DPHA, 0.02 wt% 4-methoxyphenol, 60.54 wt% NP-100, 0.41 wt% Aerosil 200 and 0.61 wt% vinyltrimethoxysilane. The base composition did not contain Ir-184 and CPI 6976, since these compounds are not needed for the rheology tests. Presence or absence of photoinitiators does not substantially change the rheology behavior of the resins. Absence of photoinitiators has the advantage of increased light stability of the resins during preparation and run of the rheology samples. Addition of 0.66 wt% Ir-184 and 3.79 wt% CPI 6976 gives UV-radiation curable resins, that can be cured with UV-radiation from for example a solid state laser. It is within the ability of the skilled man to change the amounts of photoinitiator to obtain the optimum photoresponse (like cure depth (D_p)) for his experiments.

Different amounts of thixotropic agents and flow aid are added to the base composition. Flow properties (yield stress, viscosity at shear rates 1, 10 and 100 (sec^{-1}) and filler settling speed) are measured according to the procedures mentioned before. The results are summarized below.

Sample ID:	Flowaid ID	Flow aid wt%	Anti-settling ID	Anti-settling wt%	Yield Stress (Pa)	Viscosity at shear rate 1 s ⁻¹ (Pa-s)	Viscosity at shear rate 10 s ⁻¹ (Pa-s)	Viscosity at shear rate 100 s ⁻¹ (Pa-s)	Settling Speed (mm/day)
C1.1		0,00	Thix-ST	0,50	725	2000	200	25	0.33
C1.2		0,00	Thix-ST	1,00	1200	4000	450	50	0
C1.3		0,00	Thix-ST	1,25	1500	4500	500	60	0
C1.4		0,00	Thix-ST	2,00	5000	6000	700	70	0
C1.5		0,00	Thix-ST	2,50	6200	7000	1000	150	0
1.1	M-2100	0,03	Thix-ST	1,50	0	450	70	9	0
1.2	M-2100	0,15	Thix-ST	1,50	0	450	70	9	0
1.3	M-2100	0,03	Thix-ST	3,00	1000	1200	175	20	0
1.4	M-2100	0,15	Thix-ST	3,00	400	900	100	12	0
1.5	M-2100	0,20	Thix-ST	3,00	250	700	100	12	0
1.6	LG-99	0,03	Thix-ST	1,50	1000	4000	447	50	0
1.7	LG-99	0,15	Thix-ST	1,50	200	2350	288	35	0
1.8	LG-99	0,03	Thix-ST	3,00	3000	6000	709	85	0
1.9	LG-99	0,15	Thix-ST	3,00	900	3200	457	65	0
1.10	LG-99	0,20	Thix-ST	3,00	400	2100	302	43	0
C1.6		0,00	Th-R	0,50	350	1,500	335	75	0.56
C1.7		0,00	Th-R	1,00	710	2,100	454	98	0.21
C1.8		0,00	Th-R	1,25	950	3,200	620	120	0
C1.9		0,00	Th-R	2,00	2100	4,000	762	145	0
C1.10		0,00	Th-R	2,50	3000	5,000	949	180	0
1.11	M-2100	0,03	Th-R	1,50	245	1500	365	89	0
1.12	M-2100	0,15	Th-R	1,50	0	1000	255	65	0
1.13	M-2100	0,03	Th-R	3,00	1235	1890	439	102	0
1.14	M-2100	0,15	Th-R	3,00	560	1300	314	76	0
1.15	M-2100	0,20	Th-R	3,00	317	1100	271	67	0
1.16	LG-99	0,03	Th-R	1,50	380	1790	438	107	0
1.17	LG-99	0,15	Th-R	1,50	150	1520	362	86	0
1.18	LG-99	0,03	Th-R	3,00	3200	3100	670	145	0
1.19	LG-99	0,15	Th-R	3,00	672	1910	426	95	0
1.20	LG-99	0,20	Th-R	3,00	490	1020	291	83	0

Thix-ST = Thixatrol ST

Th-R = Thixin R

M-2100 = Modalow 2100

Most of the samples did not show any settling, except for samples C1, C6 and C7.

- 5 Development of settling occurred as indicated below:

Sample ID :	In the beginning (0 day)	After 1 day (mm)	After 2 day (mm)	After 3 day (mm)	After 4 day (mm)	After 8 day (mm)	After 15 day (mm)	Gradient of the regression line (mm/day)
C1.1	0	0	0	1	1,4	2,6	4,9	0.33
C1.6	0	0.6	1.1	1.7	2.2	4.5	8.4	0.56
C1.7	0	0.6	0.4	0.6	0.8	1.7	3.2	0.21
All other exp.	0	0	0	0	0	0	0	0

Example 2----Effect of Thixotropic Reagent And Flow Aid on Recovery Time

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The recovery time of resins according to the invention is studied. 8 compositions from the example 1 have been subjected to a shear experiment, wherein the recovery of viscosity is studied by repeating the shear experiment after a certain recovery time.

example	Resin composition from exp.	Shear rate (1/S)	Time for Steady shear	Recovery time (Second)	Time for steady shear (Second)	Recovery time (Second)	Recovery Index
2.1	1.1	116	1	55	60	76	1.38
2.2	1.2	116	1	78	60	112	1.44
2.3	1.11	116	1	66	60	123	1.86
2.4	1.12	116	1	85	60	167	1.96
2.5	1.6	116	1	105	60	198	1.89
2.6	1.7	116	1	134	60	258	1.93
2.7	1.16	116	1	128	60	236	1.84
2.8	1.17	116	1	152	60	278	1.83

What is claimed is:

1. A viscosity reducible radiation curable composition comprising at least one radiation curable component and a filler, wherein the composition has the properties:
 - i) a yield stress value of < 1100 Pa,
 - 5 ii) a viscosity (at a shear rate of 1 sec^{-1}) between 1 and 1500 Pa.sec, and
 - iii) a filler settling speed less than 0.3 mm/day.
2. A viscosity reducible radiation curable composition comprising at least one radiation curable component and a filler, wherein the composition has the properties:
 - i) a yield stress value of < 1100 Pa,
 - 10 ii) a viscosity (at a shear rate of 10 sec^{-1}) between 1 and 200 Pa.sec, and
 - iii) a filler settling speed less than 0.3 mm/day.
- 3 The radiation curable composition according to claim 1 or 2, wherein the yield stress value is < 500 Pa.
- 4 The radiation curable composition according to anyone of claims 1 to 3, wherein
- 15 the composition comprises at least one photoinitiator.
- 5 The radiation curable composition according to anyone of the preceding claims, wherein the composition has a thixotropic index of at least 3.
- 6 The radiation curable composition according to anyone of the preceding claims, wherein the composition contains a thixotropic agent.
- 20 7 The radiation curable composition according to claim 6, wherein the thixotropic agent is selected from the group consisting of Thixcin R, Thixatrol 1, Thixatrol GST, Thixatrol ST, Aluminum stearate 132 and 22, MPA 14, Ken react LICA 38 and KR 55.
8. The radiation curable composition according to claim 6, wherein the
- 25 thixotropic agent is selected from the group consisting of Thixcin R, Thixatrol 1, Thixatrol GST, and Thixatrol ST.
- 9 The radiation curable composition according to anyone of the preceding claims, wherein the composition comprises a flow aid.
- 10 The radiation curable composition according to claim 9, wherein the flow agent is
- 30 selected from the group consisting of polyacrylates and polyalkyleneoxide modified polydimethylsiloxane.
- 11 The radiation curable composition according to claim 9, wherein the flow agent comprises Modaflow 2100.

12 The radiation curable composition according to anyone of the preceding claims, wherein the composition retrieves the viscosity after a steady shear of 1 second within 300 seconds.

13 The radiation curable composition according to anyone of the preceding claims, wherein the composition comprises cationically curable components, and radically curable components.

14 The radiation curable composition according to claim 9, wherein the composition comprises between 30 and 90 wt% of cationically curable components.

15 The radiation curable composition according to any one of the preceding claims, wherein the composition comprises between 5 and 50 wt% of radically polymerizable components.

16 A viscosity reducible radiation curable composition comprising 5-70 wt% of a difunctional epoxy compound

0.1-15 wt% of an acrylate having a functionality of larger than 2

0.1-10 wt% of a thixotropic agent

0.01-5 wt% of a flow modifier

10-90 wt% of a filler and

at least one photoinitiator

17 The composition according to claim 16, wherein the composition has the properties:

i) a yield stress value of < 1000 Pa,

ii) a viscosity (at a shear rate of 1 sec⁻¹) between 0 and 1500 Pa.sec, and

iii) a filler settling speed less than 0.3 mm/day.

18 A method for forming a three dimensional object comprising the steps of:

a) coating a layer of a viscosity reduced composition as define in anyone of claims 1-16 on a surface;

b) allowing said layer to become a viscosity reducible composition layer having a viscosity greater than said viscosity reduced layer;

c) exposing said viscosity reducible layer to radiation imagewise by radiation means in order to photoform said layer imagewise;

d) repeating steps a) through c) until the three dimensional object is being formed.